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(54) 【発明の名称】 複合半導体組成物とその製造方法

(57) 【要約】

【課題】 半導体粉体の粒界に微粒子が固定された構造を持ち、電場や光などで励起された半導体粉体から粒界の微粒子に電子が流れ込むことによって複合半導体の非直線抵抗性を著しく大きくすることができる複合半導体組成物とその製造方法を提供する。

【解決手段】 微粒子化した銅もしくは／そして銅酸化物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体との焼成体からなる複合半導体組成物あり、上記半導体粉体1モルに対して銅もしくは／そして銅酸化物の微粒子0.01～1モルが固着している。

【特許請求の範囲】

【請求項1】 微粒子化した銅もしくは／そして銅酸化物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体との焼成体であり、上記半導体粉体1モルに対して銅もしくは／そして銅酸化物の微粒子0.01～1モルを固着したことを特徴とする複合半導体組成物。

【請求項2】 微粒子化した銅もしくは／そして銅酸化物を高分子内に凝集させることなく分散させて得られた高分子複合物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体を混合し、これを焼成することにより、上記半導体粉体1モルに対して銅もしくは／そして銅酸化物の微粒子0.01～1モルを固着したことを特徴とする複合半導体組成物の製造方法。

【請求項3】 請求項2記載の高分子複合物は、分子の末端あるいは側鎖にシアノ基、アミノ基、そしてチオール基から選ばれた少なくとも1種の官能基を有する高分子あるいはオリゴマーの膜を作製し、この膜の上に銅を蒸着して銅もしくは／そして銅酸化物の微粒子として膜中に分散させて得られたものである複合半導体組成物の製造方法。

【請求項4】 請求項2記載の高分子複合物は、分子量を400～7,000の範囲に制限するように合成ポリアミドを重合した後、これを溶剤に溶かしたものを基板上に成膜し、この膜の上に銅を蒸着して銅もしくは／そして銅酸化物の微粒子として膜中に分散させて得られたものである複合半導体組成物の製造方法。

【請求項5】 分子量を400～7,000の範囲に制限するように重合した合成ポリアミドは、 $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{COOH}$ (n は1～36)の分子式で示されるアミノ酸モノマーと、 $\text{R}-(\text{CH}_2)_m-\text{NH}_2$ (m は1～36、 R は CH_3 、シアノ基、アミノ基、そしてチオール基から選ばれる基)で示される分子末端にアミン基を有するアミンあるいはポリアミン、また該アミンあるいはポリアミンの側鎖にシアノ基、アミノ基、そしてチオール基から選ばれる官能基を少なくとも1つ以上有するアミンあるいはポリアミンから選ばれた少なくとも1種の重合抑制剤とを触媒の存在下に重合したものである請求項4記載の複合半導体組成物の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は複合半導体組成物とその製造方法に係り、詳しくは電圧と電流特性において優れた非直線抵抗性を有し、感度を増大したガスセンサーや触媒能が向上する光触媒等に使用できる複合半導体組成物とその製造方法に関する。

【0002】

【従来の技術】 従来、 Fe_3O_4 、 SnO_2 、 TiO_2 のような半導体粉体物単体では、大きな非直線抵抗性は

有しておらず、半導体として用いるには不十分であった。この非直線抵抗性は試料に与える電場の増大に伴って励起された電子が増大して電流が増大する特性を有するもので、半導体性能を見る目安の一つになっている。また、最近では貴金属の微粒子を高分子内に凝集させることなく分散させた高分子複合物と液状の有機基を有するチタン化合物とを有機溶剤で混合して得られた組成物を基材に塗布し、有機溶剤を除去した後、熱処理して酸化チタン膜を作製する方法（特許番号第2714927号）も提案されている。

【0003】 また、分子の末端あるいは／そして側鎖のシアノ基、アミノ基、そしてチオール基から選ばれた少なくとも1種の官能基をもった高分子あるいはオリゴマーの膜の上に金を蒸着して、金の微粒子が分散した高分子複合物を作製し、この複合物を溶剤あるいは水に溶かして微粒子分散液にし、この中に酸化チタン等の担体を投入し、この担体を高分子あるいはオリゴマーの分解温度以上で焼くことにより、金微粒子を酸化チタン等に固定する方法が開発されている。このように、金微粒子を酸化チタンに担持する試みが多くなされている。

【0004】 更には、 Fe_3O_4 、 SnO_2 、 TiO_2 のような半導体に銅イオンを打ち込むイオン注入法も試みられている。

【0005】

【発明が解決しようとする課題】 しかし、従来のように微粒子を酸化チタンに担持する試みが多くなされているが、主に金などの貴金属微粒子を担持する方法であって銅系については見あたらない。これはCuもしくは Cu_2O の微粒子が安定的に得られないためである。また、イオン注入法は装置が大がかりで処置量も少なく、また粉体の処理には適さないため、実用的でなかった。本発明はこのような問題点を改善するものであり、半導体粉体の粒界に微粒子が固定された構造を持ち、電場や光などで励起された半導体粉体から粒界の微粒子に電子が流れ込むことによって複合半導体の非直線抵抗性を著しく大きくすることができる複合半導体組成物とその製造方法を提供する。

【0006】

【課題を解決するための手段】 即ち、本願の請求項1記載の発明では、微粒子化した銅もしくは／そして銅酸化物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体との焼成体であり、上記半導体粉体1モルに対して銅もしくは／そして銅酸化物の微粒子0.01～1モルを固着した複合半導体組成物にある。

【0007】 本願の請求項2記載の発明では、微粒子化した銅もしくは／そして銅酸化物を高分子内に凝集させることなく分散させて得られた高分子複合物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体を混合し、これを焼成することによ

り、上記半導体粉体1モルに対して銅もしくは／そして銅酸化物の微粒子0.01~1モルを固着した複合半導体組成物の製造方法にある。

【0008】本願の請求項3記載の発明では、請求項2記載の高分子複合物が、分子の末端あるいは側鎖にシアノ基、アミノ基、そしてチオール基から選ばれた少なくとも1種の官能基を有する高分子あるいはオリゴマーの膜を作製し、この膜の上に銅を蒸着して銅もしくは／そして銅酸化物の微粒子として膜中に分散させて得られたものである複合半導体組成物の製造方法にある。

【0009】本願の請求項4記載の発明では、請求項2記載の高分子複合物が、分子量を400~7,000の範囲に制限するように合成ポリアミドを重合した後、これを溶剤に溶かしたものを基板上に成膜し、この膜の上に銅を蒸着して銅もしくは／そして銅酸化物の微粒子として膜中に分散させて得られたものである複合半導体組成物の製造方法にある。

【0010】本願の請求項5記載の発明では、分子量を400~7,000の範囲に制限するように重合した合成ポリアミドは、 $H_2N-(CH_2)_nCOOH$ (n は1~36)の分子式で示されるアミノ酸モノマーと、 $R-(CH_2)_m-NH_2$ (m は1~36、 R は CH_3 、シアノ基、アミノ基、そしてチオール基から選ばれる基)で示される分子末端にアミン基を有するアミンあるいはポリアミン、また該アミンあるいはポリアミンの側鎖にシアノ基、アミノ基、そしてチオール基から選ばれる官能基を少なくとも1つ以上有するアミンあるいはポリアミンから選ばれた少なくとも1種の重合抑制剤とを触媒の存在下に重合した複合半導体組成物の製造方法にある。

【0011】

【発明の実施の形態】ここで使用する高分子複合物は、熱力学的に非平衡化した高分子層を作製し、この高分子層の表面に少なくとも銅を密着した後、上記高分子層を加熱して高分子層を安定化させることで該銅から粒径が100nm以下、好ましくは1~50nmの微粒子化した銅もしくは／そして銅酸化物(Cu_2O)になって高分子内に凝集させることなく分散させて得られたものである。

【0012】まず、上記高分子複合物を得る場合において、高分子層を熱力学的に非平衡化した状態に成形する必要がある。具体的には、これは高分子を真空中で加熱して融解し蒸発させて基板の上に高分子層を固化する真空蒸着方法、あるいは高分子を融解温度以上で融解し、この状態のまま直ちに液体窒素等に投入して急冷し、基板の上に高分子層を付着させる融解急冷固化方法などがある。

【0013】そのうち真空蒸着方法の場合には、通常の真空蒸着装置を使用して 10^{-4} ~ 10^{-6} Torrの真空度、蒸着速度0.1~100 μm /分、好ましくは0.

5~5 μm /分で、ガラス等の基板の上に高分子層を得ることができる。融解急冷固化方法では、高分子を融解し、該高分子固有の臨界冷却速度以上の速度で冷却して高分子層を得る。このようにして得られた高分子層は熱力学的に不安定な非平衡化した状態におかれ、時間の経過につれて平衡状態へ移行する。

【0014】本発明で使用する高分子は、例えばナイロン6、ナイロン66、ナイロン11、ナイロン12、ナイロン69、ポリエチレンテレフタレート(PET)、ポリビニルアルコール、ポリフェニレンスルフィド(PPS)、ポリスチレン(PS)、ポリカーボネート、ポリメチルメタクリレート等であって、分子凝集エネルギーとして2000cal/モル以上有するものが好ましい。この高分子は、通常言われている結晶性高分子や非晶性高分子も含む。尚、分子凝集エネルギーについては、日本化学会編 化学便覧応用編(1973年発行)の第890頁に詳細に定義されている。

【0015】続いて、前記熱力学的に非平衡化した高分子層は、その表面に銅を密着させる工程へと移される。この工程では真空蒸着装置によって銅を高分子層に蒸着させるか、もしくは銅板を直接高分子層に密着させる等の方法で銅を高分子層に積層させる。

【0016】上記銅と高分子層とが密着した複合物を、高分子のガラス転移点以上、流動温度以下の温度で加熱して高分子層を安定状態へ移行させる。その結果、銅は100nm以下で、1~50nmの領域に粒子径分布の最大をもつ銅もしくは／そして銅酸化物(Cu_2O)の微粒子となって高分子層内へ拡散浸透し、この状態は高分子層が完全に安定するまで続き、高分子層に付着していた銅の層はその厚さも減少して最終的に無くなる。上記銅もしくは／そして銅酸化物(Cu_2O)の微粒子は凝集することなく高分子層内に分布している。この場合、微粒子の含有量は0.01~90重量%であるが、この含有量は高分子層の作製条件を変えたり、銅の膜厚みを変えることによって調節ができる。

【0017】尚、本発明では、高分子複合物の製造方法は上記の方法だけでなく、例えば熔融気化法に属する気相法、沈殿法に属する液相法、固相法、分散法で銅もしくは／そして銅酸化物(Cu_2O)の微粒子を作製し、この微粒子を溶液あるいは融液からなる高分子と機械的に混合する方法、あるいは高分子と銅もしくは／そして銅酸化物(Cu_2O)とを同時に蒸発させ、気相中で混合する方法等がある。

【0018】また、本発明の高分子複合物の製造方法としては、分子の末端あるいは側鎖にシアノ基、アミノ基、そしてチオール基から選ばれた少なくとも1種の官能基を有する高分子あるいはオリゴマーの膜を作製し、この膜の上に銅を蒸着し銅もしくは／そして銅酸化物(Cu_2O)の微粒子として膜中に分散させるができる。

【0019】上記高分子あるいはオリゴマーは、分子の末端あるいは側鎖にシアノ基（ $-\text{CN}$ ）、アミノ基（ $-\text{NH}_2$ ）、そしてチオール基（ $-\text{SH}$ ）から選ばれた少なくとも1種の官能基を有するもので、その骨格にはポリエチレンオキサイド、ポリエチレングリコール、ポリビニルアルコール、ナイロン11、ナイロン6、ナイロン66、ナイロン6.10、ポリエチレンテレフタレート、ポリスチレン等からなり、その融点あるいは軟化点は $40\sim 100^\circ\text{C}$ である。オリゴマーの平均分子量も特に制限はないが、 $500\sim 3,000$ 程度である。上記官能基は特に微粒子の表面の銅もしくは／そして銅酸化物（ Cu_2O ）と共有結合や配位結合を形成しやすく、粒成長を抑制し、微粒子の分散性を高めることになる。

【0020】また、上記以外の膜2の作製方法としては、分子量を $400\sim 7,000$ の範囲に制限するように合成ポリアミドを重合した後、これを溶剤に溶かしたものを基板上に成膜することもできる。この場合、分子量が 400 未満になると、合成ポリアミドが減圧中での金属あるいは金属酸化物の蒸着時に蒸発しやすくなり、また $7,000$ を越えると、微粒子の分散が起りにくくなる。

【0021】分子量の測定方法は、ゲルパーミュエーションクロマトグラフ装置（島津製作所社製）を使用し、クロロホルムあるいはクロロホルムとメタクレゾールの重量比4対1を移動相として、ゲルパーミュエーションクロマトカラムにより得られた合成ポリアミドを分離分析し、標準資料として市販されている分子量既知のポリスチレンとの保持時間との比較により、合成ポリアミドの分子量を求めた。

【0022】具体的には、上記合成ポリアミドの作製方法としては、 $\text{H}_2\text{N}-(\text{CH}_2)_n\text{COOH}$ （ n は $1\sim 36$ ）の分子式で示されるアミノ酸モノマーと、 $\text{R}-(\text{CH}_2)_m-\text{NH}_2$ （ m は $1\sim 36$ 、 R は CH_3 、 $-\text{シアノ基}$ 、 $-\text{アミノ基}$ 、そしてチオール基から選ばれる基）で示される分子末端にアミン基を有するアミンあるいはポリアミン、また該アミンあるいはポリアミンの側鎖にシアノ基、アミノ基、そしてチオール基から選ばれる官能基を少なくとも1つ以上有するアミンあるいはポリアミンから選ばれた少なくとも1種の重合抑制剤と、触媒等を N -メチルピロリジン、ジメチルアセトアミド等の溶剤を入れ、これを攪拌しながら $100\sim 150^\circ\text{C}$ まで上昇させて窒素ガスを流しながら重合させ、重合終了後、室温まで冷却する。反応生成物を酢酸エチル、トルエン、ヘキサン等に注いで、一昼夜放置して沈殿させた後、沈殿物を濾過して集め、これを洗浄した後、 $40\sim 70^\circ\text{C}$ で乾燥した。

【0023】上記 $\text{H}_2\text{N}-(\text{CH}_2)_n\text{COOH}$ （ n は $1\sim 36$ ）の分子式で示されるアミノ酸モノマーとしては、代表的なものとして11-アミノウンデカン酸、9-

-アミノノナン酸がある。

【0024】上記重合抑制剤としては、 $\text{R}-(\text{CH}_2)_m-\text{NH}_2$ （ m は $1\sim 36$ 、 R は CH_3 、 $-\text{シアノ基}$ 、 $-\text{アミノ基}$ 、そしてチオール基から選ばれる基）で示される分子末端にアミン基を有するアミンあるいはポリアミン、また該アミンあるいはポリアミンの側鎖にシアノ基、アミノ基、そしてチオール基から選ばれる官能基を少なくとも1つ以上有するアミンあるいはポリアミンから選ばれたものであり、具体的にはヘキサメチレンジアミン、 ϵ -アミノカプロニトリル、エチレンジアミン等が使用される。

【0025】また、触媒としては、キノリン、トリフェニルホスファイト等が使用される。

【0026】また、本発明で使用する半導体粉体は Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種であり、その粉末径が $0.1\sim 10\mu\text{m}$ である。

【0027】本発明では、得られた高分子複合物をジメチルイミダゾリジノン、メタクレゾール、ジメチルホルムアミド、カルビトール、タービノール、ジアセトンアルコール、トリエチレングリコール、パラキシレン等の高沸点の有機溶剤に混合し溶解してペーストにした後、これに半導体粉体を均一に分散し、乾燥して乾燥粉にする。また、高分子複合物と半導体粉体を混合し、これに有機溶剤で溶解してペーストにした後、乾燥して乾燥粉にする。この乾燥粉を型に入れ加圧することにより予備成形し、これを空気中あるいは窒素雰囲気中、もしくは減圧中で $500\sim 900^\circ\text{C}$ 以上で $15\sim 60$ 分焼成し、所望の複合半導体組成物を得ることができる。無論、予備成形する必要はなく、乾燥粉を直接焼成することができる。

【0028】本発明の焼成した複合半導体組成物において、半導体粉体[A]は通常僅かな非直線電気抵抗性を示すが、銅もしくは／そして銅酸化物の微粒子[B]を粒界に固定することによって、複合半導体組成物 $[\text{AB}_x]$ は電場で励起された電子が粒界を通じて微粒子に流れ込み、極めて大きな非直線電気抵抗性を示すようになる。この場合、半導体粉体[A]と銅もしくは／そして銅酸化物の微粒子[B]の混合比は、[A]が1モルに対して[B]が $0.01\sim 1$ モルの範囲であり、[B]の添加量が 0.01 モル未満の場合には、励起された電子が流れた電子が流れ込む微粒子相が少なくなるために半導体特性を示さなくなり、一方1モルを越えると微粒子相が多くなって連続相となるため電子の流れ込む効果がなくなり、半導体特性を示さなくなる。

【0029】

【実施例】次に、本発明を具体的な実施例により更に詳細に説明する。

実施例1～5、比較例1～5

（高分子複合物の作製）真空蒸着装置を用いて、ナイロ

ン11のポリマーペレット5gをタングステンボード中に入れ、 10^{-6} Torrに減圧する。次いで、電圧を印加してタングステンボードを真空中で加熱してポリマーを融解させ、取り付け台の上部に設置した基板（ガラス板）上に、 $10^{-4}\sim 10^{-6}$ Torrの真空度で約 $1\mu\text{m}$ /分の速度で厚さ約 $5\mu\text{m}$ の蒸着膜の高分子層を得た。この高分子層の分子量は前記ポリマーペレットの $1/2\sim 1/10$ 程度になっている。

【0030】更に、銅チップをタングステンボード中に入れて加熱融解して $10^{-4}\sim 10^{-6}$ Torrの真空度で蒸着を行って高分子層の上に銅の蒸着膜を付着させた。これを真空蒸着装置から取り出し、 120°C に保持した恒温槽中に10分間放置して複合物を得た。その結果、この高分子複合物には層が33重量%含有し、その平均粒径は 5nm であった。得られた高分子複合物とメタクレゾールとを重量比1:1の割合で混合して、高分子複合物溶液を作製した。

【0031】（複合半導体組成物 $[\text{AB}_x]$ の作製）次に、高分子複合物溶液の所定量に、半導体粉体 $[\text{A}]$ の所定量を混合し、この混合物を 70°C で減圧中で2日間乾燥した。乾燥した混合粉体の所定量を円盤状のモールドに入れ、プレス成型機で加圧して厚さ 1mm の円盤

状の予備成形体を作製した。この予備成形体を 600°C 減圧下で3.0分間焼成した。焼成試料のサイズは直径 12mm 、厚さ 1mm であった。表1に複合半導体組成物の組成を示す。

【0032】また、得られた焼成試料の電気抵抗特性評価と非直線電気抵抗性値を求めた。その結果を表1に示す。尚、電気抵抗特性評価と非直線電気抵抗性の評価方法は以下の通りである。

【0033】電気抵抗特性評価方法は、円盤状試料の上下両面に銀ペーストを塗布して電極とし、リード線を取り付けた。2本のリード線にポテンシオスタットを用いて段階的（ 2V 間隔）に電圧を印加していき、その際の電流値を計測した。最高電圧は 20V であった。

【0034】非直線電気抵抗性値の決め方は、求めた電流-電圧特性から、電流と電圧が正比例するときの 20V 印加時の電流を1として、各試料の 20V 時の電流を割合で示した。従って、この値（非直線電気抵抗性値）が大きければ大きいほど非直線性が大きいことになり、反対に1に近ければ直線電気抵抗性（オーミック）と言うことになる。

【0035】

【表1】

	実 施 例				
	1	2	3	4	5
半導体粉体の種類	Fe_2O_3	Fe_2O_3	Fe_2O_3	SnO_2	TiO_2
半導体粉体の配合量(モル)	1	1	1	1	1
微粒子の配合量(モル)	0.01	0.1	1	0.1	0.1
非直線電気抵抗性値	102	248	153	135	176
	比 較 例				
	1	2	3	4	5
半導体粉体の種類	Fe_2O_3	Fe_2O_3	Fe_2O_3	SnO_2	TiO_2
半導体粉体の配合量(モル)					
微粒子の配合量(モル)	0	0.005	1.5	0	0
非直線電気抵抗性値	1.1	2.5	8.6	1.4	1.8

【0036】この結果、実施例の複合半導体組成物は、非直線電気抵抗性値が大きく、優れた半導体特性を示していることが判る。

【0037】実施例6

（高分子複合物の作製）分子の末端をジアミノ化した平均分子量 2000 （GCP測定による）のポリエチレンオキシドをアセトンに溶かして 20 重量%の溶液を作製した。この溶液を基材であるガラスに塗布して乾燥させると、ポリエチレンオキシドの数ミクロンの厚みの塗膜が得られた。

【0038】ガラスに保持された塗膜を電子ビーム蒸発源をもった槽内を予め 60°C に加熱した真空蒸着装置内に設置し、 5×10^{-5} 程度の真空度に調節した後、真

空蒸着装置内に設置されたるつぼ内の銅を、電子ビームを用いて加熱し、蒸発させた。蒸発した銅はポリエチレンオキシドの塗膜上に堆積した。水晶振動子上で 30nm の厚みになるように銅の蒸発量を調節した。

【0039】真空蒸着装置内を大気圧に戻して、ガラスに保持されたポリエチレンオキシドを取り出した。ポリエチレンオキシド上に堆積した銅は、堆積と同時にポリエチレンオキシドのアミノ基と化学結合して数 nm の微粒子の状態で保持され、塗膜は黄緑色の呈した。尚、銅酸化物微粒子の分散を均一にするため、窒素気流中、 60°C で加熱した。

【0040】また、ガラスより銅酸化物微粒子を分散したポリエチレンオキシドを剥ぎ取り、水に浸けると、

これは溶けて黄緑色を呈した銅酸化物微粒子の分散水溶液が得られた。この水溶液は安定しており、1ヵ月放置しても黄緑色は消えなかった。

【0041】得られた高分子複合物とメタクレゾールとを重量比1:1の割合で混合して、高分子複合物溶液を作製した。

【0042】(複合半導体組成物 $[AB_x]$ の作製)次に、粉体半導体 Fe_3O_4 1モルに高分子複合物溶液の銅酸化物微粒子が0.1モルになるように混合し、この混合物を70°Cで減圧中で2日間乾燥した。乾燥した混合粉体の所定量を円盤状のモールドに入れ、プレス成型機で加圧して厚さ1mmの円盤状の予備成形体を作製した。この予備成形体を600°C減圧下で30分間焼成した。焼成試料のサイズは直径12mm、厚さ1mmであった。表1に複合半導体組成物の組成を示す。

【0043】また、得られた焼成試料の電気抵抗特性評価と非直線電気抵抗性値を求めた。その結果を表2に示す。

【0044】

【表2】

	実施例 6
半導体粉体の種類	Fe_3O_4
半導体粉体の配合量(モル)	1
微粒子の配合量(モル)	0.1
非直線電気抵抗性値	275

【0045】この結果、実施例の複合半導体組成物は、非直線電気抵抗性値が大きく、優れた半導体特性を示していることが判る。

【0046】

【発明の効果】以上のように本願請求項1記載の発明では、微粒子化した銅もしくは/そして銅酸化物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体との焼成体であり、上記半導体粉体1モルに対して銅もしくは/そして銅酸化物の微粒子0.01~1モルを固着した複合半導体組成物にあり、非直線電気抵抗性値が大きく、優れた半導体特性を示す効果がある。

【0047】また、本願請求項2~5記載の発明では、微粒子化した銅もしくは/そして銅酸化物を高分子内に凝集させることなく分散させて得られた高分子複合物と Fe_3O_4 、 SnO_2 、そして TiO_2 から選ばれた少なくとも1種の半導体粉体を混合し、これを焼成することにより、上記半導体粉体1モルに対して銅もしくは/そして銅酸化物の微粒子0.01~1モルを固着した複合半導体組成物の製造方法にあり、非直線電気抵抗性値が大きく、優れた半導体特性を示す効果がある。

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CLAIMS

[Claim 1] the copper or/and the copper acid ghost which atomized, Fe 3O₄, SnO₂, and TiO₂ from - compound semi-conductor constituent which is a baking object with at least one sort of selected semi-conductor fine particles, and is characterized by fixing 0.01-1 mol of particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles.

[Claim 2] The macromolecule composite and Fe 3O₄ which were distributed without making the copper or/, and the copper acid ghost which atomized condense in a macromolecule, and were obtained, SnO₂ and TiO₂ from - the manufacture approach of the compound semi-conductor constituent characterized by fixing 0.01-1 mol of particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles by mixing at least one sort of selected semi-conductor fine particles, and calcinating this.

[Claim 3] A giant-molecule composite according to claim 2 is the manufacture approach of the compound semi-conductor constituent which produces the giant molecule which has at least one sort of functional groups chosen as the end or side chain of a molecule from a cyano group, the amino group, and a thiol group, or the film of oligomer, vapor-deposits copper on this film, is distributed in the film as a particle of copper or/, and a copper acid ghost, and is obtained.

[Claim 4] A macromolecule composite according to claim 2 is the manufacture approach of the compound semi-conductor constituent which forms on a substrate what melted this to the solvent, vapor-deposits copper on this film, is distribute in the film as a particle of copper or/, and a copper acid ghost, and is obtain after carry out the polymerization of the synthetic polyamide so that molecular weight may be restrict to the range of 400-7,000.

[Claim 5] The synthetic polyamide which carried out the polymerization so that molecular weight might be restricted to the range of 400-7,000 The amino acid monomer shown with the molecular formula of H₂N-(CH₂)_n-COOH (n is 1-36), R-(CH₂)_m-NH₂ (m - 1-36 R - CH₃-) The amine or polyamine which has an amine radical at the molecule end shown by the cyano group, the amino group, and the radical chosen from a thiol group, To the side chain of this amine or polyamine, moreover, a cyano group, amino group, And the manufacture approach of the compound semi-conductor constituent according to claim 4 which carries out the polymerization of at least one sort of polymerization retarders chosen from the amine or polyamine which has at least one or more functional groups chosen from a thiol group to the bottom of existence of a catalyst.

DETAILED DESCRIPTION

[0001]

[Field of the Invention] This invention relates to a compound semi-conductor constituent and its manufacture approach, has the nonlinear resistance which was excellent in the electrical potential difference and the current characteristic in detail, and relates to the compound semi-conductor constituent which can use sensibility for the photocatalyst the gas sensor which increased, and whose catalyst ability improve, and its manufacture approach.

[0002]

[Description of the Prior Art] The former, Fe₃O₄, SnO₂, and TiO₂ The semi-conductor fine-particles object simple substance [like] of big nonlinear resistance was inadequate for not having but using as a semi-conductor. This nonlinear resistance has the property that the electron excited with increase of the electric field given to a sample increases, and a current increases, and has become one of the standards which look at the semi-conductor engine performance. Moreover, after applying to a base material the constituent which mixed the giant-molecule composite distributed without making the particle of noble metals condense in a giant molecule recently, and the titanium compound which has a liquefied organic radical by the organic solvent, and was obtained and removing an organic solvent, the approach (patent number No. 2714927) of heat-treating and producing the titanium oxide film is also proposed.

[0003] moreover, the end of a molecule or/, the cyano group of a side chain, and the amino group - and ***** from a thiol group -- the approach of fixing a golden particle to titanium oxide etc. is developed by vapor-depositing gold on a macromolecule with one sort of functional groups, or the film of oligomer, even if few, producing the macromolecule composite which the golden particle distributed, melting this composite in a solvent or water, making it particle dispersion liquid, supplying support, such as titanium oxide, in this, and burning this support above a macromolecule or the decomposition temperature of oligomer. Thus, many attempts which support a golden particle to titanium oxide are made.

[0004] Furthermore, Fe₃O₄, SnO₂, and TiO₂ The ion-implantation which drives a copper ion into a semi-conductor [like] is also tried.

[0005]

[Problem(s) to be Solved by the Invention] However, although many attempts which support a particle to titanium oxide like before are made, it is the approach of mainly supporting noble-metals particles, such as gold, and is not found about a copper system. This is because the particle of Cu or Cu₂O is not obtained stably. Moreover, its equipment was large-scale, there were also few amounts of treatment, and since ion-implantation was not suitable for processing of fine particles, it was not practical. This invention improves such a trouble and has the structure where the particle was fixed to the grain boundary of semi-conductor fine particles, and when an electron flows into the particle of a grain boundary from the semi-conductor fine particles excited with electric field, light, etc., the compound semi-conductor constituent which can enlarge nonlinear resistance of a compound semi-conductor remarkable, and its manufacture approach are offered.

[0006]

[Means for Solving the Problem] namely, the copper or/and the copper acid ghost which atomized in invention of this application according to claim 1, Fe₃O₄, SnO₂, and TiO₂ from -- it is a baking object with at least one sort of selected semi-conductor fine particles, and is in the compound semi-conductor constituent which fixed 0.01-1 mol of particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles.

[0007] The macromolecule composite and Fe₃O₄ which were distributed without making the copper or/, and the copper acid ghost which atomized condense in a macromolecule in invention of this application according to claim 2, and were obtained, SnO₂ and TiO₂ from -- it is in the manufacture approach of the compound semi-conductor constituent which fixed 0.01-1 mol of

particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles by mixing at least one sort of selected semi-conductor fine particles, and calcinating this.

[0008] In invention of this application according to claim 3, a giant-molecule composite according to claim 2 produces the giant molecule which has at least one sort of functional groups chosen as the end or side chain of a molecule from a cyano group, the amino group, and a thiol group, or the film of oligomer, and is in the manufacture approach of the compound semi-conductor constituent which vapor-deposits copper on this film, is distributed in the film as a particle of copper or/, and a copper acid ghost, and is obtained.

[0009] In invention of this application according to claim 4, after a macromolecule composite according to claim 2 carry out the polymerization of the synthetic polyamide so that molecular weight may be restrict to the range of 400-7,000, what melted this to the solvent be form on a substrate, and it be in the manufacture approach of the compound semi-conductor constituent which vapor-deposit copper on this film, be distribute in the film as a particle of copper or/, and a copper acid ghost, and be obtain.

[0010] The synthetic polyamide which carried out the polymerization in invention of this application according to claim 5 so that molecular weight might be restricted to the range of 400-7,000 The amino acid monomer shown with the molecular formula of $H_2N-(CH_2)_nCOOH$ (n is 1-36), $R-(CH_2)_m-NH_2$ ($m = 1-36$, $R = CH_3$), The amine or polyamine which has an amine radical at the molecule end shown by the cyano group, the amino group, and the radical chosen from a thiol group, Moreover, it is in the manufacture approach of the compound semi-conductor constituent which carried out the polymerization of at least one sort of polymerization retarders chosen as the side chain of this amine or polyamine from the amine or polyamine which has a cyano group, an amino group, and at least one or more functional groups chosen from a thiol group to the bottom of existence of a catalyst.

[0011]

[Embodiment of the Invention] The macromolecule composite used here produces the macromolecule layer which un-equilibrated thermodynamically. Particle size from this copper by heating the above-mentioned macromolecule layer and stabilizing a macromolecule layer, after sticking copper to the front face of this macromolecule layer at least 100nm or less, It is made to distribute, without becoming 1-50nm the copper or/, and the copper acid ghost (Cu_2O) which atomized preferably, and making it condense in a macromolecule, and is obtained.

[0012] First, when obtaining the above-mentioned macromolecule composite, it is necessary to fabricate in the condition of having un-equilibrated the macromolecule layer thermodynamically. The vacuum deposition approach which this is heated, and a macromolecule is dissolved, and it evaporates it in a vacuum, and specifically solidifies a macromolecule layer on a substrate, or a macromolecule is dissolved above a melting out temperature, and it supplies to liquid nitrogen etc. immediately with this condition, and quenches, and there is the fusion quenching solidification approach of making a macromolecule layer adhering on a substrate etc.

[0013] Among those, using the usual vacuum evaporation system, by 10 degree of vacuum [of $-4 - 10^{-6}$ Torr] and evaporation rate [of 0.1-100 micrometers /], it is a part for 0.5-5-micrometer/preferably, and, in the case of the vacuum deposition approach, a macromolecule layer can be obtained on substrates, such as glass. By the fusion quenching solidification approach, a macromolecule is dissolved, it cools the rate more than the critical cooling rate of this macromolecule proper, and a macromolecule layer is obtained. Thus, the obtained macromolecule layer is thermodynamically set in the unstable condition of having un-equilibrated, and shifts to equilibrium along with the passage of time.

[0014] The macromolecules used by this invention are nylon 6, Nylon 66, Nylon 11, Nylon 12, nylon 69, polyethylene terephthalate (PET), polyvinyl alcohol, a polyphenylene sulfide (PPS), polystyrene (PS), a polycarbonate, polymethylmethacrylate, etc., and what it has more than 2000cal / mol as molecule cohesive energy is desirable. This macromolecule also contains the crystalline polymer and amorphous polymer which are usually said. In addition, about molecule cohesive energy, he is the edited by Chemical Society of Japan. It is defined as the 890th page edited (1973 issue) by chemistry handbook application by the detail.

[0015] Then, the macromolecule layer which un-equilibrated on said thermodynamics target is moved to the process which sticks copper on the front face. At this process, a macromolecule layer is made to vapor-deposit copper with a vacuum evaporation system, or the laminating of the copper is carried out to a macromolecule layer by the approach of sticking a copper plate in a direct macromolecule layer.

[0016] The composite which the above-mentioned copper and a macromolecule layer stuck is heated at the temperature below flow temperature more than the glass transition point of a macromolecule, and a macromolecule layer is made to shift to a stable state. Consequently, copper is 100nm or less, it becomes the particle of the copper which has the max of particle size distribution in a 1-50nm field or/, and a copper acid ghost (Cu_2O), and diffusion osmosis is carried out into a macromolecule layer, it continues until a macromolecule layer is completely stabilized by this condition, that thickness also decreases and, finally the layer of the copper adhering to a macromolecule layer is lost. The particle of the above-mentioned copper or/, and a copper acid ghost (Cu_2O) is distributed in a macromolecule layer, without condensing. In this case, although the content of a particle is 0.01 - 90 % of the weight, accommodation of this content is possible by changing the production conditions of a macromolecule layer or changing copper film thickness.

[0017] in addition, in this invention, the manufacture approach of a macromolecule composite not only in the above-mentioned approach For example, the gaseous-phase method belonging to the melting evaporating method, the liquid phase process belonging to settling, a solid phase technique, The particle of copper or/, and a copper acid ghost (Cu_2O) is produced with a variational method, the approach of mixing this particle with the macromolecule which consists of a solution or melt on a machine target or a macromolecule, copper or/, and a copper acid ghost (Cu_2O) are evaporated in coincidence, and there is the approach of mixing in a gaseous phase etc.

[0018] Moreover, the macromolecule which has at least one sort of functional groups chosen as the end or side chain of a molecule from a cyano group, the amino group, and a thiol group as the manufacture approach of the macromolecule composite of this invention, or the film of oligomer is produced, and although copper is vapor-deposited on this film and it is made to distribute in the film as a particle of copper or/, and a copper-acid ghost (Cu_2O), it can do.

[0019] The above-mentioned macromolecule or oligomer has at least one sort of functional groups chosen as the end or side chain of a molecule from a cyano group (-CN), the amino group (-NH₂), and a thiol group (-SH), and becomes the frame from polyethylene oxide, a polyethylene glycol, polyvinyl alcohol, Nylon 11, nylon 6, Nylon 66, nylon 6.10, polyethylene terephthalate, polystyrene, etc., and the melting point or softening temperature is 40-100-degreeC. Although especially a limit does not have the average molecular weight of oligomer, either, it is 500 to about 3,000. Especially the above-mentioned functional group will tend to form the copper or/, the copper acid ghost (Cu_2O) and the surface covalent bond, and surface coordinate bond of a particle, will control grain growth, and will raise the dispersibility of a particle.

[0020] Moreover, after carrying out the polymerization of the synthetic polyamide as the production approach of film 2 other than the above so that molecular weight may be restricted to the range of 400-7,000, what melted this to the solvent can also be formed on a substrate. In this case, if

molecular weight becomes less than 400, it will become [which a synthetic polyamide is decompressing] easy to evaporate at the time of vacuum evaporation of a metal or a metallic oxide, and if 7,000 is exceeded, distribution of a particle will stop being able to happen easily. [0021] Gel par MYUESHON chromatograph equipment (Shimadzu Corp. make) was used for the measuring method of molecular weight, it carried out separation analysis of the synthetic polyamide obtained by the gel par MYUESHON chromatographic column by having made the weight ratio 4 to 1 of chloroform or chloroform, and the metacresol into the mobile phase, and calculated the molecular weight of a synthetic polyamide by the comparison with the holding time with the polystyrene of molecular weight known marketed as standard data.

[0022] Specifically as the production approach of the above-mentioned synthetic polyamide The amino acid monomer shown with the molecular formula of $H_2N-(CH_2)_nCOOH$ (n is 1-36), $R-(CH_2)_m-NH_2$ (m -- 1-36R -- CH_3 -) The amine or polyamine which has an amine radical at the molecule end shown by the cyano group, the amino group, and the radical chosen from a thiol group, Moreover, at least one sort of polymerization retarders chosen as the side chain of this amine or polyamine from the amine or polyamine which has a cyano group, an amino group, and at least one or more functional groups chosen from a thiol group, Solvents, such as N-methyl pyrrolidine and dimethylacetamide, are put in for a catalyst etc., it is made to go up to 100-150-degreeC, the polymerization of the nitrogen gas is carried out with a sink, stirring this, and it cools to a room temperature after polymerization termination. Ethyl acetate, toluene, a hexane, etc. were filled with the resultant, and after having filtered and collected precipitate after leaving it one whole day and night and making it precipitate, and washing this, it dried by 40-70-degreeC.

[0023] As an amino acid monomer shown with the molecular formula of above-mentioned $H_2N-(CH_2)_nCOOH$ (n is 1-36), 11-amino undecanoic acid and 9-amino nonoic acid are typical.

[0024] as the above-mentioned polymerization retarder -- $R-(CH_2)_m-NH_2$ (m -- 1-36R -- CH_3 -) The amine or polyamine which has an amine radical at the molecule end shown by the cyano group, the amino group, and the radical chosen from a thiol group, Moreover, it is chosen as the side chain of this amine or polyamine out of the amine or polyamine which has a cyano group, an amino group, and at least one or more functional groups chosen from a thiol group. Specifically, a hexamethylenediamine, epsilon-amino capronitrile, ethylenediamine, etc. are used.

[0025] Moreover, a quinoline, triphenyl phosphite, etc. are used as a catalyst.

[0026] Moreover, the semi-conductor fine particles used by this invention are at least one sort chosen from Fe_3O_4 , SnO_2 , and TiO_2 , and the diameter of powder is 0.1-10 micrometers.

[0027] In this invention, after mixing and dissolving in the organic solvent of high-boiling points, such as dimethyl imidazolidinone, the metacresol, dimethylformamide, carbitol, TAPI Norian, diacetone alcohol, triethylene glycol, and paraxylene, and making a paste the obtained giant-molecule composite, to this, semi-conductor fine particles are distributed to homogeneity, and it dries, and is made desiccation powder. Moreover, after mixing semi-conductor fine particles with a macromolecule composite, dissolving in this by the organic solvent and making it a paste, it dries and is made desiccation powder. It preforms by putting this desiccation powder into a mold and pressurizing it, and this can be under reduced pressure among air or nitrogen-gas-atmosphere mind, it can calcinate for 15 to 60 minutes above 500-900-degreeC, and a desired compound semi-conductor constituent can be obtained. Of course, it is not necessary to preform and desiccation powder can be calcinated directly.

[0028] In the compound semi-conductor constituent which this invention calcinated, although semi-conductor fine particles [A] show few [usually] nonlinear electric resistance nature, by fixing the particle [B] of copper or/, and a copper acid ghost to a grain boundary, the electron excited in electric field flows into a particle through a grain boundary, and a compound semi-conductor

constituent [ABx] comes to show very big nonlinear electric resistance nature. In this case, the mixing ratio of the particle [B] of semi-conductor fine particles [A], copper or/, and a copper acid ghost When [A] is the range whose [B] is 0.01-1 mol to one mol and the addition of [B] is less than 0.01 mols Since a particle phase will increase and it will become a continuous phase if it stops showing a semi-conductor property and one mol is exceeded on the other hand, since the particle phase into which the electron with which the excited electron flows decreases, the effectiveness that an electron flows in is lost, and it stops showing a semi-conductor property.

[0029]

[Example] Next, a concrete example explains this invention to a detail further.

Using one to examples 1-5 and example of comparison 5 (production of a macromolecule composite) vacuum evaporation system, polymer pellet 5g of Nylon 11 is put in into a tungsten board, and it decompresses to 10^{-6} Torr. Subsequently, the electrical potential difference was impressed, the tungsten board was heated in the vacuum, the polymer was dissolved, and the macromolecule layer of the vacuum evaporation film with a thickness of about 5 micrometers was obtained the rate for about 1-micrometer/on the substrate (glass plate) installed in the upper part of a mount with the degree of vacuum of 10^{-4} - 10^{-6} Torr. The molecular weight of this macromolecule layer has become about 1 of said polymer pellet / two to 1/10.

[0030] Furthermore, the copper chip was put in into the tungsten board, heating fusion was carried out, it vapor-deposited with the degree of vacuum of 10^{-4} - 10^{-6} Torr, and the copper vacuum evaporation film was made to adhere on a macromolecule layer. This was taken out from the vacuum evaporation system, in the thermostat held to 120-degreeC, it was left for 10 minutes and the composite was obtained. Consequently, in this macromolecule composite, the layer contained 33% of the weight, and that mean particle diameter was 5nm. The macromolecule composite and metacresol which were obtained were mixed at a rate of the weight ratio 1:1, and the macromolecule composite solution was produced.

[0031] (Production of a compound semi-conductor constituent [ABx]) Next, the specified quantity of semi-conductor fine particles [A] was mixed to the specified quantity of a macromolecule composite solution, this mixture was under reduced pressure by 70-degreeC to it, and it dried for two days to it. The specified quantity of dry mixed fine particles was put into disc-like mold, it pressurized with the press briquetting machine, and the disc-like preforming object with a thickness of 1mm was produced. This preforming object was calcinated for 30 minutes under 600-degreeC-reduced pressure. The size of a baking sample was 1mm in the diameter of 12mm, and thickness. The presentation of a compound semi-conductor constituent is shown in Table 1.

[0032] Moreover, the electric resistance characterization and the nonlinear electric resistance nature value of a baking sample which were acquired were calculated. The result is shown in Table 1. In addition, the evaluation approach of electric resistance characterization and nonlinear electric resistance nature is as follows.

[0033] The electric resistance characterization approach applied the silver paste, used it as the electrode, and attached lead wire in vertical both sides of a disc-like sample. two lead wire – a potentiostat – using – being gradual (2V spacing) – the electrical potential difference is impressed and the current value in that case was measured. The maximum voltage was 20V.

[0034] From the current-voltage characteristic searched for, how to decide a nonlinear electric resistance nature value set the current at the time of 20V impression in case a current and an electrical potential difference are in direct proportion to 1, and showed the current at 20 V:00 of each sample at a rate. Therefore, if nonlinearity will be large and is closer to 1 on the contrary as this value (nonlinear electric resistance nature value) is large, it will be called straight-line electric resistance nature (ohmic).

[0035]
[Table 1]

[0036] Consequently, the compound semi-conductor constituent of an example has a large nonlinear electric resistance nature value, and it turns out that the outstanding semi-conductor property is shown.

[0037] The polyethylene oxide of the mean molecular weight 2000 (based on GPC measurement) which diamino-ized the end of example 6 (production of a giant-molecule composite) molecule was melted to the acetone, and 20% of the weight of the solution was produced. When the glass which is a base material was made to apply and dry this solution, the paint film with a thickness [of polyethylene oxide] of several microns was obtained.

[0038] After installing in the vacuum evaporation system which heated beforehand the inside of the tub which had an electron beam evaporation source for the paint film held at glass to 60-degreeC and adjusting to about 5xten to five degree of vacuum, using the electron beam, the copper in the crucible installed in the vacuum evaporation system was heated, and was evaporated. The copper which evaporated was deposited on the paint film of polyethylene oxide. Copper evaporation was adjusted so that it might become the thickness of 30nm on a quartz resonator.

[0039] The inside of a vacuum evaporation system was returned to the atmospheric pressure, and the polyethylene oxide held at glass was taken out. the chemical bond of the copper deposited on polyethylene oxide is carried out to the amino group of deposition, simultaneously polyethylene oxide, and it is held in the state of a several nm particle -- having -- a paint film -- yellowish green -- having presented . In addition, in order to make distribution of a copper acid ghost particle into homogeneity, it heated by 60-degreeC among the nitrogen air current.

[0040] Moreover, when the polyethylene oxide which distributed the copper acid ghost particle was stripped off and it soaked in water from glass, the distributed water solution of the copper acid ghost particle which this melted and presented yellowish green was obtained. This water solution was stable, and even if it left it for one month, yellowish green did not disappear.

[0041] The macromolecule composite and metacresol which were obtained were mixed at a rate of the weight ratio 1:1, and the macromolecule composite solution was produced.

[0042] (Production of a compound semi-conductor constituent [ABx]) Next, it mixed so that the copper acid ghost particle of a macromolecule composite solution might become 0.1 moles to fine-

particles semi-conductor Fe_3O_4 1 mol, and this mixture was under reduced pressure by 70-degreeC, and it dried for two days. The specified quantity of dry mixed fine particles was put into disc-like mold, it pressurized with the press briquetting machine, and the disc-like preforming object with a thickness of 1mm was produced. This preforming object was calcinated for 30 minutes under 600-degreeC reduced pressure. The size of a baking sample was 1mm in the diameter of 12mm, and thickness. The presentation of a compound semi-conductor constituent is shown in Table 1.

[0043] Moreover, the electric resistance characterization and the nonlinear electric resistance nature value of a baking sample which were acquired were calculated. The result is shown in Table 2.

[0044]

[Table 2]

[0045] Consequently, the compound semi-conductor constituent of an example has a large nonlinear electric resistance nature value, and it turns out that the outstanding semi-conductor property is shown.

[0046]

[Effect of the Invention] the copper which atomized by invention of this application claim 1 publication as mentioned above, or/— and a copper acid ghost, Fe_3O_4 , SnO_2 , and TiO_2 from — it is a baking object with at least one sort of selected semi-conductor fine particles, and it is in the compound semi-conductor constituent which fixed 0.01-1 mol of particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles, and a nonlinear electric resistance nature value is large, and there is effectiveness which shows the outstanding semi-conductor property.

[0047] moreover, the copper which atomized in invention of two to this application claim 5 publication or/— and the macromolecule composite and Fe_3O_4 which were distributed without making a copper acid ghost condense in a macromolecule, and were obtained, SnO_2 , and TiO_2 from — by mixing at least one sort of selected semi-conductor fine particles, and calcinating this It is in the manufacture approach of the compound semi-conductor constituent which fixed 0.01-1 mol of particles of copper or/, and a copper acid ghost to the one mol of the above-mentioned semi-conductor fine particles, and a nonlinear electric resistance nature value is large, and there is effectiveness which shows the outstanding semi-conductor property.

CLAIMS

[Claim 1] Titanium oxide particle;; light catalytic particle which is equipped with at least one sort of metals or the alloy which covers the front face of said titanium oxide particle so that a part of front face of said titanium oxide particle may be exposed, and which is chosen from silver, copper, zinc, and nickel, and is characterized by the particle size of the; aforementioned titanium oxide particle being 1 micrometer or less.

[Claim 2] The light catalytic particle according to claim 1 characterized by said alloy containing both copper, or both [one side or] only a total of ten to 50% of the weight further including silver.

[Claim 3] Said metal or alloy is a light catalytic particle according to claim 1 or 2 characterized by being covered by the front face of said titanium oxide particle in the shape of discontinuity film.

[Claim 4] The light catalytic particle according to claim 1 to 3 characterized by the particle size of said metal or an alloy being 0.1 micrometers or less.

[Claim 5] The light catalytic particle according to claim 1 to 4 to which the weight ratio to said light catalytic particle of said covered metal or an alloy is characterized by being 1 - 20%.

DETAILED DESCRIPTION

[0001]

[Field of the Invention] This invention is used for disassembly of dirt, such as decomposition of the oil which adhered to the cooking appliance etc. especially, and a sheathing material, deodorization, immobilization of a carbon dioxide, etc. about the light catalytic particle which has a photocatalyst operation, and relates to a suitable light catalytic particle.

[0002]

[Description of the Prior Art] Conventionally, using gamma-manganese oxide as a catalyst, the approach (heat catalyst) of heating an oil together with this and promoting the perfect combustion of an oil and titanium oxide were applied to support, such as a steel plate and a filter, and the approach by the photocatalyst which decomposes oil has been used for disassembly of an oil by irradiating ultraviolet rays at this. Since especially a photocatalyst does not need to hold an object to an elevated temperature on the occasion of decomposition like a heat catalyst, need is increasing quickly in recent years. Moreover, it was also known that what carried out the ion implantation of the transition metals, such as Cr, to titanium oxide has a photocatalyst operation in a light region. Furthermore, the optical-pumping effectiveness is checked also with the organic semiconductive polymer excited on the wavelength comparatively near a light region.

[0003]

[Problem(s) to be Solved by the Invention] However, if it was not ultraviolet rays, in order that a

catalysis might not break out, since the ultraviolet ray lamp was needed and ultraviolet rays were used for the inorganic system photocatalyst represented by the above titanium oxide in use, it also had to take the optical cutoff to the body into consideration. Moreover, the photocatalyst using an ion implantation had the high manufacturing cost, and it was difficult to use it for a large area practically. On the other hand, the problem of not being so strong as an oil and dirt being disassembled had the optical-pumping effectiveness of an organic semiconductive polymer.

[0004] Then, this invention aims at offering the light catalytic particle which was excellent in the photocatalyst property and was especially excellent in the photocatalyst property in a light field.

[0005]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as shown in drawing 1, the light catalytic particle 1 by invention concerning claim 1 is equipped with at least one sort of metals or the alloy 3 which covers surface 2a of the titanium oxide particle 2 so that a part of surface 2a of the titanium oxide particle 2 and; titanium oxide particle 2 may be exposed and which is chosen from silver, copper, zinc, and nickel, and is characterized by for the particle size of; titanium oxide particle 2 to be 1 micrometer or less.

[0006] Thus, if constituted, since a part of surface 2a of the titanium oxide particle 2 will be exposed Since it has at least one sort of metals or the alloy 3 which the photocatalyst activity of titanium oxide is discovered in the part exposed especially, and is chosen from silver, copper, zinc, and nickel Since it is easily excited by the exposure of the light of wavelength shorter than a light region or it, an electron and an electron hole are produced and it is in the condition which can move in an electron or an electron hole between a metal or an alloy 3, and titanium oxide 2 in the covered part The electron or electron hole produced with the metal or the alloy 3 is supplied to titanium oxide. Moreover, since the particle size of titanium oxide is 1 micrometer or less, a quantum size effect is produced.

[0007] By this light catalytic particle, it is [like] good also as a thing according to claim 2 in which an alloy 3 contains both copper, or both [one side or] only a total of ten to 50% of the weight further including silver.

[0008] With such a configuration, since an alloy 3 contains both copper, or both [one side or] only a total of ten to 50% of the weight further including silver, it excels especially in an oil solution property.

[0009] A thing [that the metal or the alloy 3 is covered with the above light catalytic particles by surface 2a of the titanium oxide particle 2 in the shape of discontinuity film like] according to claim 3 is desirable.

[0010] With such a configuration, since the metal or the alloy 3 is covered by surface 2a of the titanium oxide particle 2 in the shape of discontinuity film, a part of front face of a titanium oxide particle exposes it.

[0011] further – being according to claim 4 – like – a light catalytic particle according to claim 1 to 3 – the particle size of a metal or an alloy 3 – 0.1 micrometers or less – it is – making – a thing is desirable.

[0012] Moreover, it is desirable that the weight ratio to the light catalytic particle 1 of the metal covered with the light catalytic particle according to claim 1 to 4 like or an alloy according to claim 5 constitutes so that it may be 1 - 20%.

[0013] Since the weight ratio to the light catalytic particle 1 of a metal or an alloy is 1 - 20% at this time, the coat of a metal or an alloy can cover minutely the shape of discontinuity film, the shape of for example, an island, and the sufficient electron and sufficient electron hole for titanium oxide are supplied, it excels in the decomposition property of an oil or dirt.

[0014]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 is the extension mimetic diagram having taken out and shown the light catalytic particle by this invention only one piece. In practice, the impalpable powder which consists of such a light catalytic particle is used as a catalyst. As shown in drawing 1, the light catalytic particle by the gestalt of operation of this invention has covered the metal or the alloy 3 so that the part may be exposed to surface 2a of the titanium oxide 2 which is the base material which carried out the globular form mostly.

[0015] It excites in an ultraviolet radiation region, and it covers with the gestalt of 1 operation of this invention in the shape of discontinuity film (the shape of an island [Especially]) so that a part of front face of titanium oxide may expose the metal or alloy which uses at least one or more sorts in silver, copper, zinc, and nickel as a main component to the titanium oxide particle which discovers an oil solution property etc.

[0016] If these metals or alloys 3 are covered by the titanium oxide particle 2, an oxide will be formed in the front face or the surface section of the oxygen for example, in the atmospheric air which exists on the outskirts. At this time, the whole does not need to oxidize [the covered metal or alloy] to the interior, and only the front face or the surface section of covering should oxidize. Moreover, even if all the surface areas of covering do not oxidize, it is also good for a part to oxidize.

[0017] Thus, the metal formed in the front face or the surface section of covering or the scaling object of an alloy has a semi-conductor property. For example, it is 1.2eV, and the band gap in the room temperature in the case of the silver oxide (Ag_2O) is very narrow compared with 3.2eV of that of titanium oxide, it is easily excited by the exposure of a light of wavelength shorter than a light region or it, and produces an electron and an electron hole by it.

[0018] Through a silver coat, a part of electron emitted from the silver oxide here and electron hole are supplied to the titanium oxide which is a base material, and it is the front face of titanium oxide, and it is multiplied by the electron and electron hole which it is excited by the ultraviolet rays included in the lights, such as sunlight, and are generated, and promotes the photocatalyst activity of titanium oxide. Furthermore, since these metals or alloys have the catalyst effectiveness which oxidizes the organic substance also in itself, they discover an operation of the oil solution which was excellent with these two effectiveness.

[0019] That is, a part of front face of titanium oxide is exposed, and the coat [activity / alloy / the metal which uses at least one or more sorts of silver, copper, zinc, and nickel as a main component, or] is minutely covered with the other part, and, moreover, this coat is covered with the gestalt of operation of this invention by the condition which can move in titanium oxide, an electron, or an electron hole.

[0020] Moreover, since the titanium oxide which is a base material is a particle 1 micrometer or less, a quantum size effect is produced. If a titanium oxide particle is made into such magnitude and the above metals or alloys are covered by the front face in the shape of an island, these electrons and electron holes will become a reactant high thing, without receiving thermal relaxation with a grid. That is, the electron at the time of the metal or alloy covered on the surface of a particle exciting and the reactivity of an electron hole increase. Magnitude of a titanium oxide particle is desirably set to 0.5 micrometers or less. If the magnitude of the titanium oxide particle of a base material exceeds 1 micrometer, the electron and electron hole which the oxide which exists in the surface of the metal by which surface coating was carried out, or an alloy excites and generates will disappear by lattice vibration, and will stop being able to discover photocatalyst activity easily.

[0021] Said metal or alloy is covered in the shape of discontinuity film so that a part of front face of titanium oxide may be exposed to the front face of the titanium oxide which is a base material. This

is because the photocatalyst activity of titanium oxide will not be discovered if titanium oxide is completely covered with the metal or the alloy.

[0022] With the shape of discontinuity film, there are various gestalten, such as the shape of the shape of an island, a line, and a muscle and punctiform, here. Island-like covering is in the condition that the metal or the alloy is covered with one or more discontinuous film to the titanium oxide particle. When it covers in the shape of discontinuity film, the coverage (surface area of the area/titanium oxide of the part with which the metal or the alloy is covered by the titanium oxide particle) is desirably taken as 20 - 50% of range.

[0023] Moreover, the covering configurations of the metal or alloy in the case of covering the front face of a titanium oxide particle from a viewpoint of the above-mentioned discontinuity film, so that a part of front face of a titanium oxide particle may be exposed may be various gestalten, such as the shape of a line besides the shape of an island, and a muscle, and punctiform, as mentioned above. Furthermore, when the direction of radiation of light takes that it is not isotropic, either into consideration practical, as shown in drawing 1, it is desirable [with / the number of discontinuity film / one / or more / it has effectiveness, but] to cover the perimeter of a titanium oxide particle by two or more two or more discontinuity film (the case where five islands are formed in drawing 1 along with the great circle of the titanium oxide particle which carried out the globular form mostly is shown).

[0024] Moreover, in order to receive the above-mentioned electron and supply of an electron hole, titanium oxide, a metal, or an alloy is joined electrically. It is both so-called mixture, and when electric junction cannot be desired, it is hard to discover effectiveness like this invention.

[0025] It is made 1 - 20% of the weight (weight ratio) of the range of the such light catalytic particle formed [in / for example / island-like covering] in the amount of covering on the titanium oxide particle of a metal or an alloy. In this range, discontinuity film-like covering is attained and supply of enough electrons for titanium oxide and an electron hole is performed.

[0026] Moreover, mixing of the impurity in the case of covering is lessened as much as possible. Electric junction will become firm if it does in this way. Moreover, a physical vapor deposition called the vacuum deposition and sputtering which are decompressing among a vacuum as the covering approach and are processed from the point of an alloy plate is performed.

[0027] Moreover, let the amount of covering of the metal or alloy to a titanium oxide particle be 1 - 20% of the weight of the range from a viewpoint of covering minutely to the shape of an island typically from a viewpoint of covering so that a part of front face of a titanium oxide particle may be exposed. When there is a possibility that the effectiveness of a metal or an alloy plate may not show up when fewer than 1 % of the weight, and it exceeds 20 % of the weight, there is a possibility of a surface coating metal or an alloy covering a titanium oxide particle or its floc completely, and losing photocatalyst activity. Moreover, the cost rise at the time of covering also poses a problem.

[0028] Furthermore, the particle size has [the metal or alloy covered in the shape of discontinuity film (the shape of an island / Typically /) by the front face attained with the above-mentioned amount of covering] desirable 0.1 micrometers or less. This is for carrying out according to a quantum size effect that it is easy to move an electron and an electron hole while increasing the catalytic activity which increases surface area and oxidizes the organic substance by very fine particle-ization.

[0029] On the other hand, the titanium oxide covered has the desirable thing of the point of photocatalyst activity to an anatase mold, and especially the configuration is not limited. Moreover, when condensing remarkably, after cracking, it uses.

[0030] As mentioned above, a titanium oxide particle with a particle size of 1 micrometer or less

which covered at least one or more sorts of the metals or alloys of silver, copper, zinc, and nickel in 1 - 20% of the weight of the range in the shape of discontinuity film Industrial use is very large by the effectiveness of organic substance decomposition, such as an oil in the conventional ultraviolet-rays wavelength region, not only improving, but being able to disassemble an oil and dirt also in the long wavelength light of a light region, and covering to a steel plate or resin.

[0031] Thus, while raising the photocatalyst activity in the conventional ultraviolet-rays wavelength field to the strong titanium oxide powder of the photocatalyst effectiveness by covering the metal or alloy which uses at least one or more sorts of the silver of the specified quantity, copper, zinc, and nickel as a main component, a long wavelength side can also make photocatalyst activity appear rather than the field.

[0032] There are a nonelectrolytic plating method, physical vapor deposition, etc. in the approach of covering to a titanium oxide particle so that a part of front face of a titanium oxide particle may expose the above metals or alloys, the discontinuous shape of film, shape of for example, an island. It is desirable to use the sputtering method especially indicated by application (JP,2-153068,A) of these people's point. According to this approach, mixing of an impurity does not have generating of waste fluid etc. few again, either, and can cover a metal or an alloy efficiently in the shape of [discontinuous] film to titanium oxide powder.

[0033] By the sputtering method used here, first, fluid jet mill processing of the impalpable powder of titanium oxide is carried out in an inert atmosphere, and it distributes to a primary particle, for example. Thus, heating under reduced pressure processing of the obtained impalpable powder which carried out distributed processing is carried out in an inert atmosphere. The impalpable powder which carried out heating under reduced pressure processing is taught to the tumbler which dedicated the source of sputtering (silver, copper, zinc, nickel, or those alloys), the container is rotated, the fluid bed of impalpable powder is formed, and where a container is rotated, sputtering is carried out to flow impalpable powder. Thus, the metal or alloy of the source of sputtering is covered on the front face of a titanium oxide particle.

[0034]

[Example] The metal or the alloy was covered with the predetermined amount of covering to the titanium oxide powder of 0.5 micrometers of example 1 mean diameters. To 1g of this powder, 0.1g of salad oil was added, and it mixed, put into the glass petri dish with a diameter of 7cm by having made this into the irradiated object, and put on the sealing box gently. And with the high pressure mercury vapor lamp of 400W, light (ultraviolet) was irradiated over 7 hours from the location distant from the petri dish 250mm. In addition, the temperature rise of the irradiated object at the time of this exposure was about 120 degrees C.

[0035] The weight reduction after an exposure estimated the photocatalyst property in connection with an oil solution under these conditions. The result is shown in the table of drawing 2 and drawing 3. Evaluation carries out the oil solution only of the titanium oxide of the particle size same as comparison material by the same approach. That to which the weight reduction by this example exceeds 1.2 times rather than this weight reduction noting that especially an oil solution property is excellent O Moreover, ** was made into x noting that the property deteriorated 0.8 or less times, noting that there was no improvement in an oil solution property about what exceeds 0.8 times for O from 1.0 or less times noting that an oil solution property is excellent in 1.2 or less times in the case where 1.0 times are exceeded.

[0036] It turns out that the ingredient used by this example from these results is excellent in an oil solution property only compared with titanium oxide under UV irradiation. Moreover, it also turns out that the thing using the alloy which made silver contain 10 - 50% of the weight of copper or zinc as a surface coating layer from this example has the especially excellent property.

[0037] The same evaluation as an example 1 was performed to the same powder as example 2 example 1 using the incandescent lamp of 200W which can irradiate light with the wavelength in the range of the light from infrared radiation. The result is shown in the table of drawing 4 and drawing 5.

[0038] It turns out that the ingredient used by this example from these results excels the ingredient of only titanium oxide in the oil solution property also in the light of infrared radiation to a light field. Moreover, it also turns out that the thing using the alloy which made silver contain 10 - 50% of the weight of copper or zinc as a surface coating layer from this example has the especially excellent property.

[0039] To the titanium oxide particle which has the mean diameter of example 3 versatility, the alloy of Ag50Zn50 (a subscript shows weight %) was covered with the sputtering method so that it might become about 5 % of the weight to the done whole light catalytic particle weight. At this time, the oil solution property was investigated by the same evaluation approach as an example 1. The result is shown in drawing 6. According to this result, particle size is [evaluation] O in about 1 micrometer and about 0.7 micrometers to evaluation being [the particle size of titanium oxide] x in about 1.3 micrometers, and particle size being [evaluation] ** in about 1.15 micrometers, and particle size is [evaluation] O in about 0.5 micrometers, about 0.25 micrometers, and about 0.1 micrometers further.

[0040] It turns out that the oil solution property is excellent in titanium oxide with a particle size of 1 micrometer or less (range shown by A in drawing 6) which is in this example from these results. Moreover, it also turns out that especially the property especially is excellent in the particle size of 0.5 micrometers or less.

[0041] To the titanium oxide particle of 0.3 micrometers of example 4 mean diameters, the alloy of Ag50Cu50 (a subscript is weight %) of various weight %s was covered with the sputtering method. At this time, the same approach as an example 1 estimated the oil solution property by the difference in the amount of covering. The result is shown in drawing 7. In drawing 7, in order to shorten an axis of abscissa and to show it, the middle is omitted. According to this result, as for evaluation, weight % of evaluation of the amount of covering of an alloy is O in about 10%, about 5%, and about 3% at about 20%, about 15.7%, and about 15% at O and a pan to weight % of evaluation of the amount of covering of an alloy being x at about 20.7%. Next, as for evaluation, weight % of the amount of covering of an alloy becomes O at about 1%, and evaluation becomes ** at about 0.5%.

[0042] These results show that the amount of covering of this example is excellent in an oil solution property at 1 - 20 % of the weight (range shown by B in drawing 7). Moreover, the amount of covering is known by that especially a property especially is good at 3 - 10 % of the weight.

[0043] The alloy of Ag50Cu30Zn20 (a subscript is weight %) was covered with the sputtering method 20% of the weight to the titanium oxide particle of 1 micrometer of example 5 mean diameters, and this was heat-treated in time amount various at the temperature of 600 degrees C, and a vacuum to it. In addition, the melting point of this alloy is about 800 degrees C. At this time, the magnitude of a surface coating alloy was observed and the same approach as an example 1 estimated the relation between that particle size and an oil solution property. The result is shown in drawing 8. In addition, the axes of abscissa of drawing 8 are logarithmic scale. According to this result, the particle size of evaluation of an alloy is O in about 0.1 micrometers, about 0.035 micrometers, and about 0.016 micrometers to the particle size of an alloy being [evaluation] O in about 0.3 micrometers.

[0044] These results show having a good oil solution property especially in the range shown by C in drawing 8, when the particle size of a surface alloy particle is 0.1 micrometers or less.

[0045] As mentioned above, according to the gestalt of operation of this invention, the improvement in a property of a titanium oxide photocatalyst can be brought about, and the oil solution property in a light field can be raised especially remarkably. These light catalytic particle begins cookware and a kitchen instrument with self-cleaning nature, the application to sheathing, interior building materials, etc. is possible for it, and the contribution to industrialization is very large. Moreover, the photocatalyst material by this invention can only be used for various fields, such as disassembly of not only an oil solution but nitrogen oxides, or a sulfur oxide, disassembly of organic substance dirt, antibacterial, and carbon-dioxide immobilization.

[0046]

[Effect of the Invention] It has at least one sort of metals or the alloy which covers the front face of a titanium oxide particle so that a part of front face of this particle may be exposed to the titanium oxide particle excited in an ultraviolet radiation region according to this invention as mentioned above and which is chosen from silver, copper, zinc, and nickel, and it becomes possible to offer the light catalytic particle which was excellent in the photocatalyst property and was especially excellent in the photocatalyst property in a light field since the particle size of said titanium oxide particle was 1 micrometer or less.